Recovery of Rare Earths from Magnet Sludge by FeCl$_2$

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A large amount of neodymium magnet sludge is generated during the manufacture process. Because the sludge is considerably contaminated by oxygen, it is difficult to reuse it as it is. The present basic study has been carried out to establish efficient recycling process of the sludge. The rare earths in the neodymium magnet sludge were extracted by chlorination with FeCl$_2$. An activated carbon was used as a de-oxidation reagent. Metallic iron in the sludge was not chlorinated because the iron monochloride is not stable. The extracted rare earth chlorides were easily separated from Fe-alloy and the excess of FeCl$_2$ by vacuum distillation. In this study, 96% of neodymium and 94% of dysprosium in the sludge were extracted into chloride phase. By the vacuum distillation, a mixture of neodymium and dysprosium trichlorides of 99.2% purity was recovered with the rare earth element's yield of 76% for the charged sludge. In addition, it was confirmed that the rare earth chlorides can be converted to the corresponding oxides by a pyrohydrolysis reaction accompanied by a formation of HCl gas. The HCl gas can chlorinate metallic iron to FeCl$_2$. Therefore, a new recycling process for rare earth magnet waste can be realized as a chlorine circulation type process. During the process, only carbon and water are consumed, and there are no toxic pollutants. Moreover, the obtained rare earth oxide can be directly used as raw material in the oxide electrolysis, which is the conventional industrial reduction process for rare earth metal production.

1. Introduction

Because sintered Fe$_{14}$Nd$_2$B based magnet is the strongest permanent magnet, it has been used in various electronic devices.[1] The magnet production is increasing by 20 percent a year. On the other hand, a large amount of magnet waste is produced during the magnet manufacture process. For example, amount of scrap yielded is only several percent relative to the raw material, while the amount of sludge (grinding and processing waste) is several tens of percent of that of the raw material.[2] The sludge is considerably contaminated by oxygen and it is difficult to reuse it as it is. Thus, developing an effective recycling process for the magnet sludge is of crucial importance.

Several wet processes for recycling the sludge has been proposed.[3–5] One of drawbacks of the processes is that they produce a large amount of wastewater. As an alternative process, other researchers have proposed a new dry recycling process for the magnet scrap by using a metallic extraction reagent such as molten magnesium or silver.[6–8] They succeeded in recovering the rare earths in metallic state as Mg or Ag alloys, and suggested that it is easy to remove magnesium from magnesium-rare earth alloys by distillation at a high temperature. Regarding to the scrap recycling, it is our belief that this method is one of the most promising methods because of its simplicity. In the case of sludge recycling, however, it is rather difficult to apply the Mg or Ag alloy extraction method due to the high level of oxygen contamination in the sludge (typically 3.8 mass%O[2]). As an alternative process applicable to the oxygen contaminated sludge, the slag-metal separation process was proposed recently.[2] But, as far as the trial results were revealed, good separation between the rare earth enriched slag phase and the iron enriched metal phase has not been developed yet. On the other hand, a recycling process based on the metal calcium de-oxidation was proposed for Sm–Co magnet waste.[9] However there is no report on the practical de-oxidation method for Nd–Fe–B magnet waste as far as we know, although some trials for developing efficient de-oxidation method are being carried out.[10]

Another recently proposed dry processes are based on chlorination of the scrap and sludge.[11,12] Murase *et al.* reported a recycling process by CVT (Chemical Vapor Transport) method combined with the sludge chlorination by chlorine gas.[11,13] The excellent separation between rare earths and iron or cobalt was demonstrated by the CVT method. Nevertheless, the inherent disadvantage of the process is unselective chlorination, which consists in that all the metallic elements in the sludge are chlorinated. Therefore, further processes for the treatment of iron chloride are necessary.

To develop a more advanced process for the sludge recycling, the problem of iron chlorination should be avoided. For this purpose, we carried out a basic study on the selective chlorination of rare earths in the neodymium magnet sludge (Fe–Nd–B system) by FeCl$_2$ and proposed a basic concept of novel recycling process for the rare earth magnet sludge.

2. Principle and Thermodynamics

2.1 Thermodynamics of chlorides

The chemical potentials of chlorine at equilibrium between a metal and the corresponding chloride, and that between lower and higher valence chlorides are calculated on the basis of available thermodynamic data.[14–16] The calculated results are plotted in Fig. 1. The chemical potential of chlorine at H$_2$/HCl equilibrium is also plotted in the figure. Among the elements shown in Fig. 1, Ni and Al are usually used as coating material for the commercial rare earth magnets. The elements such as Co, Dy and Al are used as additive elements in the neodymium magnet. As seen from Fig. 1, the chemical potentials of chlorine at equilibrium between the rare earth metals and corresponding dichlorides are considerably lower

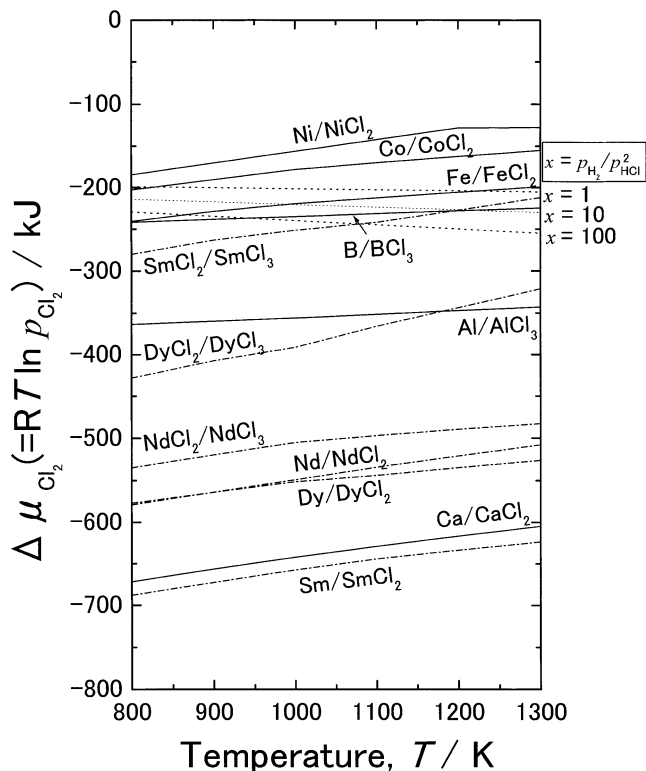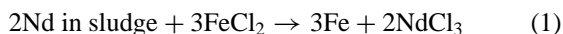*Corresponding author. E-mail: uda@tagen.tohoku.ac.jp

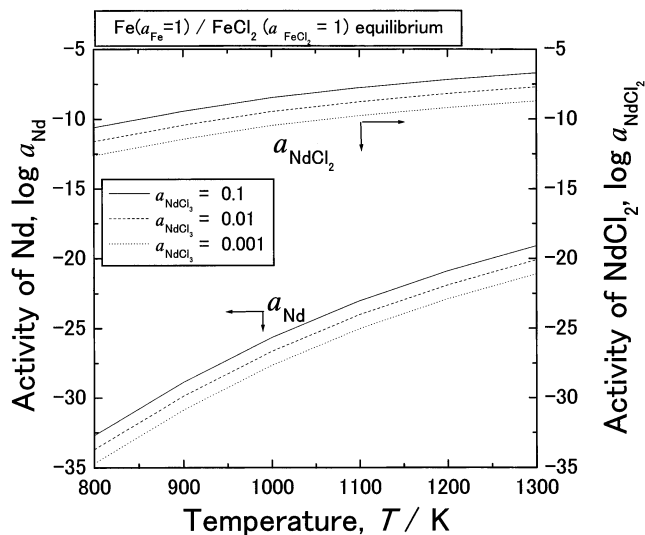Fig. 1   Chemical potential of chlorine at each equilibrium.

Fig. 2   Activities of neodymium and neodymium dichloride when the chemical potential of chlorine is fixed at $Fe/FeCl_2$ equilibrium and activity of neodymium trichloride is fixed at 0.1, 0.01 or 0.001.
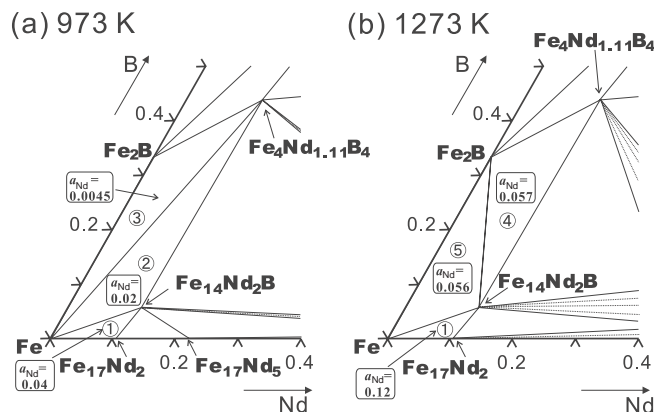

Fig. 3   Phase diagrams of iron-rich corner in the system Fe–Nd–B at 973 K and 1273 K. Activity of neodymium at each phase equilibrium is shown. Thermodynamic data assessed by Hallemans *et al.*[17] was used for calculating the neodymium activity. Activities of boron are: at 973 K, ① 4.2×10^{-5} ② 1.7×10^{-4} ③ 2.6×10^{-4}; at 1273 K, ① 4.9×10^{-4} ④ 2.2×10^{-3} ⑤ 2.2×10^{-3}.

than those at the equilibrium between the iron group metals and corresponding dichlorides. Thus, when rare earth metals coexist with the iron group metals in a metal mixture, rare earth metals can be chlorinated without any chlorination of the iron group metals if the chemical potential of chlorine in the system is kept between the equilibrium potential of $Fe/FeCl_2$ and that of $Nd/NdCl_2$. One of the simple methods to set the chemical potential of chlorine in such range is addition of $FeCl_2$ to the sludge. As the activity of iron in the neodymium magnet sludge is unity or close to unity, $Fe/FeCl_2$ equilibrium can be attained by the only addition of $FeCl_2$. Moreover, the use of $FeCl_2$ is attractive because the molten $FeCl_2$ (m.p. 950 K, b.p. 1297 K) is expected to act as a reaction medium for the chlorination reaction of rare earths in the sludge.

Figure 2 shows the activity of neodymium and neodymium dichloride calculated under the following conditions: 1 The chemical potential of chlorine is fixed at $Fe(a_{Fe} = 1)/FeCl_2(a_{FeCl_2} = 1)$ equilibrium. 2 The activity of neodymium trichloride is equal to 0.1, 0.01, or 0.001. As seen from the figure, the activity of neodymium at the equilibrium is lower than $\sim 10^{-20}$ in the temperature range from 800 to 1300 K. Thus, if the neodymium activity in the sludge is higher than $\sim 10^{-20}$, the following reaction can be expected,

$$2Nd \text{ in sludge} + 3FeCl_2 \rightarrow 3Fe + 2NdCl_3 \qquad (1)$$

Under condition of the $Fe/FeCl_2$ equilibrium, the activity of neodymium dichloride is considerably lower than that of neodymium trichloride. This suggests that the concentration of divalent neodymium in the $FeCl_2$–$NdCl_3$ molten salt can be neglected.

2.2   Thermodynamics of the system of Fe–Nd–B

We adopt the basic composition of $Fe_{14}Nd_2B$ as the composition of the neodymium magnet for the thermodynamic discussions for the sake of simplicity. Phase diagrams of iron-rich corner of the Fe–Nd–B system at 973 and 1273 K are shown in Fig. 3 together with the activity of neodymium. For the calculation of activities, thermodynamic data assessed by Hallemans *et al.*[17] are used. The data are listed in Table 1. As can be seen from the figure, the activities of neodymium at concentration lower than that of $Fe_{14}Nd_2B$ are larger than 4.5×10^{-3} at 973 K and 5.6×10^{-2} at 1273 K respectively. These values are considerably higher than the equilibrium values, $a_{Nd} = \sim 10^{-20}$, shown in Fig. 2. Therefore, it is expected that almost all neodymium of the $Fe_{14}Nd_2B$ can be extracted to molten chloride phase when the chemical potential of chlorine is fixed at $Fe/FeCl_2$ equilibrium.

2.3   Thermodynamics of the system of Ln–O–Cl

Because the magnet sludge is highly contaminated by oxygen, a part of rare earth in the sludge exists as rare earth ox-

Table 1 The standard Gibbs energy of formation, $\Delta_f G°$, of intermediate compounds in the system Fe–Nd–B at 973 K and 1273 K. These data were calculated from equations suggested by Hallemans *et al.*[17]

Phases	$\Delta_f G°$/kJ·mol^{-1}	
	973 K	1273 K
Fe$_2$B	−66.8	−64.9
Fe$_{14}$Nd$_2$B	−133.5	−126.0
Fe$_4$Nd$_{1.11}$B$_4$	−315.8	−292.8
Fe$_{17}$Nd$_2$	−51.9	−45.4

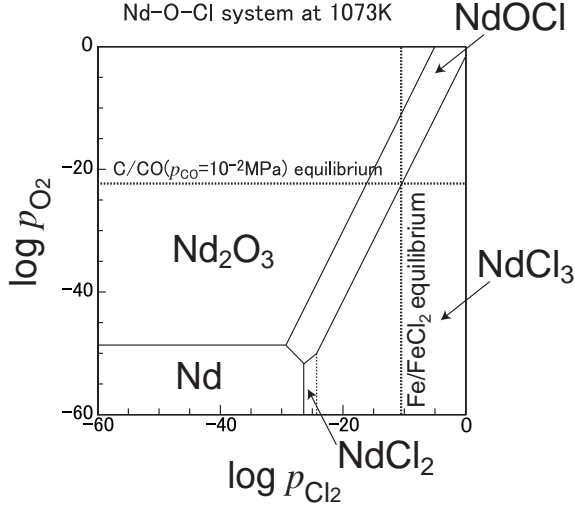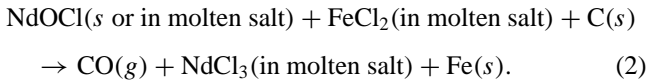Fig. 4 Chemical potential diagram for Nd–O–Cl system at 1073 K. Fe/FeCl$_2$ and C/CO ($p_{CO} = 10^{-2}$ MPa) equilibrium are also plotted.

Fig. 5 Vapor pressures of metal chlorides in the literature are plotted against inverse temperature.[14]

ides (Ln$_2$O$_3$ (Ln = rare earth element)) and/or hydroxides (Ln(OH)$_3$). The latter decomposes into Ln$_2$O$_3$ and H$_2$O at elevated temperatures. Thus, the carbochlorination method for the conversion of rare earth oxides to chlorides is applied. For the quantitative consideration, the chemical potential diagram is shown in Fig. 4 for Nd–O–Cl system at 1073 K. As seen from the figure, when the partial pressures of oxygen and chlorine are fixed at Fe/FeCl$_2$ and C/CO (the partial pressure of CO gas, p_{CO}, is less than 10^{-2} MPa) equilibrium, the stable neodymium compound is NdCl$_3$. The value of $p_{CO} = 10^{-2}$ MPa is high enough for CO gas to diffuse into an atmosphere under 0.1 MPa. Thus, the carbochlorination of NdOCl by FeCl$_2$ is expected as the following reaction,

NdOCl(s or in molten salt) + FeCl$_2$(in molten salt) + C(s)

$$\rightarrow CO(g) + NdCl_3(\text{in molten salt}) + Fe(s). \qquad (2)$$

Under conditions $p_{CO} < 10^{-2}$ MPa and $T = 1073$ K, the equilibrium partial pressure of CO$_2$ gas is less than 10^{-5} MPa.[14]

In order to confirm that reaction (2) proceeds, we carried out a series of preliminary experiments at 973 K. A mixture of neodymium oxide (Nd$_2$O$_3$), activated carbon and FeCl$_2$ was heated for 6 h under Ar atmosphere of atmospheric pressure, and then the product was recovered by a vacuum distillation. As the results, the formation of NdCl$_3$ was observed, while the formation of NdCl$_3$ was not observed without activated carbon. Therefore, the conversion of rare earth oxide in the
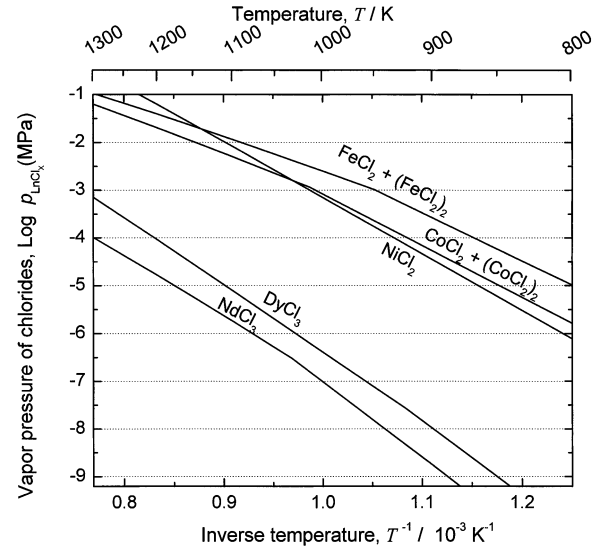
magnet sludge to the corresponding chlorides by FeCl$_2$ can be achieved by addition of carbon.

2.4 Possibility of vacuum distillation

Figure 5 presents the vapor pressures of various metal chlorides available in the literature.[14] For iron and cobalt chlorides, total vapor pressures of dichloride monomer and dimer are plotted. The vapor pressures of iron and cobalt trichlorides are also calculated with the partial pressure of chlorine at the Fe(s)/FeCl$_2$(l) or Co(s)/CoCl$_2$(l) equilibrium. The calculated pressures are considerably smaller than those of corresponding dichlorides. For example, the vapor pressure of FeCl$_3$ is 7×10^{-6} MPa at 1100 K. As seen from the figure, the vapor pressures of dichloride of the iron group elements are three orders of magnitude larger than those of rare earth trichlorides. This difference in vapor pressure ensures a possibility for the separation of the chlorides of the iron group elements from the rare earth trichlorides by the vacuum distillation, during which the dichlorides of iron group elements and the rare earth trichlorides are transferred *via* a gas phase and condense at different temperatures.

In addition to chlorination of rare earth elements in the sludge, the chlorination of aluminum and boron can be anticipated from Fig. 1 although boron may not be chlorinated extensively, because the chemical potential of chlorine at B/BCl$_3$ equilibrium is only slightly lower than that of Fe/FeCl$_2$ equilibrium and the boron activity in the sludge is low (the calculated boron activities are shown in the caption of Fig. 3). But these trichlorides of aluminum and boron are expected to be easily removed from the rare earth trichloride by distillation, because the boiling points of AlCl$_3$ and BCl$_3$ are considerably lower than that of rare earth trichlorides; AlCl$_3$ (456 K), BCl$_3$ (286 K).

Based on the above thermodynamic consideration, we adopt FeCl$_2$ as a chlorination reagent for the selective chlorination of rare earth elements in the neodymium magnet sludge.

3. Experimental

3.1 Apparatus and materials

A schematic drawing of the apparatus used for the extraction of rare earth elements combined with the vacuum distillation is shown in Fig. 6. A closed end stainless steel tube (I.D. 35 mm) was placed vertically inside a heater. The upper part of the stainless steel tube was wrapped with a heat insulator. A cold trap filled with liquid nitrogen was placed between an exhaust port and vacuum pump. A graphite crucible (I.D. 24 mm) was placed at the bottom of the stainless steel tube. Two upended graphite crucibles with $\phi 10$ mm hole were inserted inside the stainless steel tube as shown in Fig. 6. The upended graphite crucibles were used as a "lower temperature collector" and "higher temperature collector", respectively. In the distillation experiments, temperatures of the collectors were in the range from 853 to 1123 K and from 413 to 853 K respectively. A mixture of 15 g of $FeCl_2$ powder (purity 99.9%), 1.0 g of activated carbon (purity 98%) and 5.0 g of magnet sludge was placed in the graphite crucible inside a glove box under a high purity Ar atmosphere. The dried magnet sludge was obtained from Shin-Etsu Chemical Co., Ltd. The composition of the magnet sludge is 61.2%Fe–24.1%Nd–4.5%Dy–1.0%B (mass%). Aluminum and cobalt are also involved in the sludge as additional elements. The activated carbon and sludge were dried under vacuum at 473 K for 3 days before experiments.

3.2 Procedure

Before starting the experiments, the atmosphere inside the stainless steel tube was replaced by a high purity Ar gas. Then, temperature of graphite crucible was raised up to 1073 K and kept at the temperature for 12 h. Subsequently, the temperature of graphite crucible was raised up to 1273 K, and then evacuation of the stainless steel tube and distillation were started. The heater powering was cut off after the distillation of 3 h. The mass of condensate on the interior surface
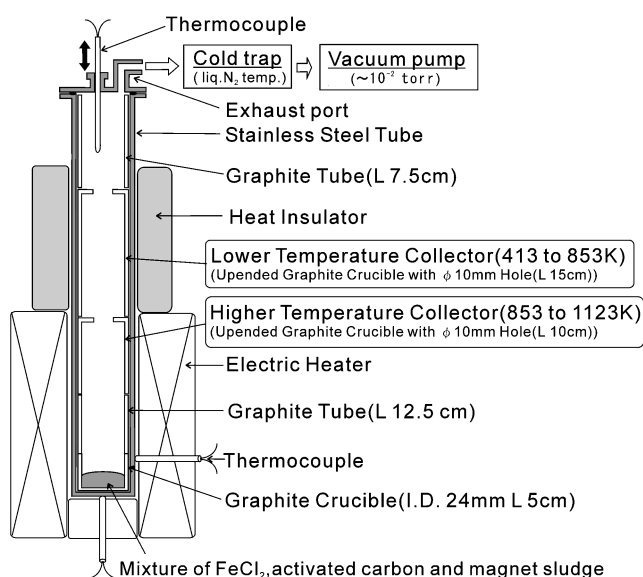

Fig. 6 Schematic diagram of apparatus for vacuum distillation of chlorides in combination with selective chlorination of rare earth elements in the magnet sludge by $FeCl_2$.

of the each collector was determined from the change in the mass of each collector after the distillation experiments. All the chlorides, deposited on the collector surfaces, were dissolved in a hot concentrated nitric acid. The residue in the graphite crucible after the experiments was removed from the crucible and ground to fine powder by an agate mortar. Then a part of the powder was dissolved in hot concentrated nitric acid. The concentrations of iron, neodymium, dysprosium and boron in the solutions were analyzed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES). In another runs, the chlorides deposited on the collector surfaces and residue in the graphite crucible were collected inside the glove box. Then, all elements in the periodic table except ones from hydrogen to oxygen were analyzed qualitatively by X-ray fluorescence analysis (XRF). The phases, presented in the residue, were identified by X-ray diffraction analysis (XRD).

4. Results and Discussion

4.1 Experimental results

The extraction and distillation experiments were carried out under various conditions. Typical results of the experiments will be discussed in detail below.

4.1.1 Condensate on the collector surface

After extraction (1073 K for 12 h under Ar-atmosphere) and vacuum distillation (1273 K for 3 h), green and gray deposits were observed inside the higher temperature collector, while a yellow ocher deposit was observed inside the lower temperature collector. The cationic mass percent of Fe, Nd, Dy and B of the higher and lower temperature deposits, and the deposit mass are shown in Table 2. It should be noted that, when the lower temperature collector was removed from the stainless steel tube, a small part of deposit fell out of the lower temperature collector into the stainless steel reaction tube so that the deposit mass of the lower temperature collector must be slightly larger than that shown in Table 2. By the qualitative XRF analysis, a trace of manganese (Mn) was found in the lower temperature deposit. The trace probably came from the stainless steel tube. No other cationic element was detected in both the higher and lower temperature deposits. The cationic mass percent of (Nd + Dy) to (Fe + Nd + Dy + B) is 99.2% in the higher temperature deposit as shown in Table 2. In the case of the lower temperature deposit, the cationic mass percent of Fe to (Fe + Nd + Dy + B) is 98.7%. Thus, we can conclude that the higher and lower temperature deposits are $LnCl_3$-enriched and $FeCl_2$-enriched chlorides, respectively. The high purity of rare earth chlorides (99.2%) in the higher temperature collector suggests that there is a possibility for producing a mixture of neodymium and dysprosium metals of 99% purity by a subsequent reduction process.

4.1.2 Residue in the graphite crucible

A black residue was obtained in the graphite crucible. The photographs of the sludge before experiment and residue after it are shown in Fig. 7. The residue is in the form of a slightly agglomerated powder. The X-ray diffraction patterns of the sludge and residue are shown in Fig. 8. In the sludge, diffraction peaks corresponding to $Fe_{14}Nd_2B$ and $Nd(OH)_3$ are observed. However, no diffraction peak corresponding to $Fe_{14}Nd_2B$ and $Nd(OH)_3$ is observed in the residue. Instead, the diffraction peaks of Bcc-Fe, graphite, Fe_3C and NdOCl

Table 2 Cationic mass percent of Fe, Nd, Dy and B in lower and higher temperature deposits.

	Cationic mass percent of Fe, Nd, Dy and B					Mass of deposit
	$c_i/(c_{Fe} + c_{Nd} + c_{Dy} + c_B) \times 100^*$					w/g
	Fe	Nd	Dy	B	(Nd + Dy)	
Higher Temperature Deposit (853 to 1123 K)	0.8	82.4	16.8	n.a.	99.2	1.86
Lower Temperature Deposit (413 to 853 K)	98.7	0.7	0.3	0.2	1.0	11.51

$*c_i$: mass% of i.

(a) Sludge as received
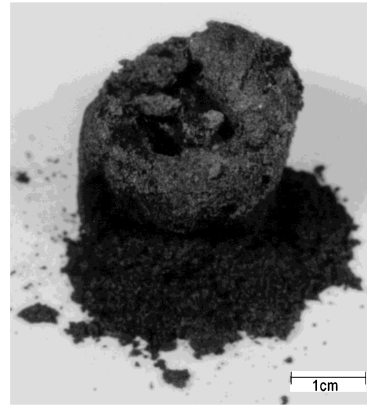

(b) Residue after experiment

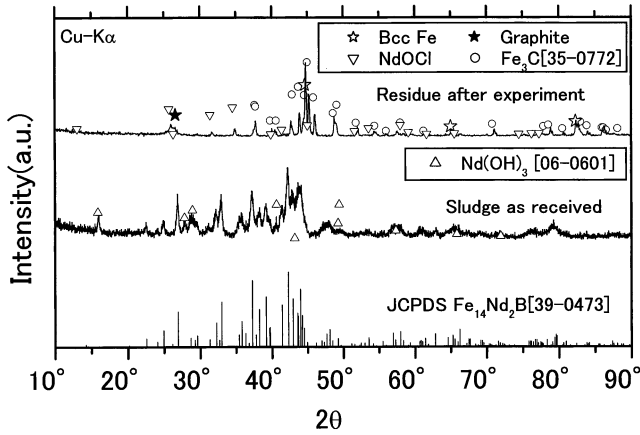Fig. 7 Photograph of initial sludge and residue after experiment.

Fig. 8 X-ray diffraction patterns of the sludge as received and residue after experiment.

Table 3 Composition and mass of Fe, Nd, Dy and B in initial sludge and residue, and extraction ratio for rare earths.

(a)	Composition of Fe, Nd, Dy and B				Other elements detected by XRF
	c_i/mass%				
	Fe	Nd	Dy	B	
Sludge	61.16	24.12	4.47	1.00	Al, Co
Residue*	79.43	0.66	0.18	0.57	Co, Cl

(b)	Mass of Fe, Nd, Dy and B				Mass of initial sludge or residue
	w_i/g ($\times 10^{-3}$ mol)				w/g
	Fe	Nd	Dy	B	
Sludge	3.058 (55.7)	1.206 (8.36)	0.224 (1.38)	0.050 (4.6)	5.000
Residue**	5.600 (102)	0.046 (0.321)	0.013 (0.080)	0.040 (3.7)	7.051

(c) Extraxtion ratio(%)	Nd	Dy	Average
	96.2	94.2	95.9

*Unreacted active carbon is included in the residue.

**The incease in the mass of iron is due to reactions caused by the reduction of FeCl₂ to Fe or Fe₃C.

are detected. The formation of metallic iron, Fe₃C, LnCl₃ and disappearance of Fe₁₄Nd₂B suggest that the reactions expressed by eqs. (1) and (2) proceeded actually.

The composition of the sludge and the residue after experiments are shown in Table 3(a). A large part of rare earth in the sludge was chlorinated and extracted. The mass percent of neodymium and dysprosium decreased to 0.66% from 24.12% and to 0.18% from 4.47%, respectively. The elements, detected in the residue and the sludge by the qualitative XRF analysis, are also listed in the table. Table 3(b) presents mass of Fe, Nd, Dy and B in the sludge and residue. As seen from Table 3(c), the extraction ratio is 96% for Nd and 94% for Dy respectively. The extraction ratio is defined

as the ratio of loss in amount of the rare earth in the graphite crucible to amount of the rare earth in the initially charged sludge. On the other hand, the mass of rare earth trichloride obtained in the higher temperature collector is 1.86 g as shown in Table 2. It is corresponding to 76% relative to the

mass of rare earth trichlorides calculated from the assumption that all the rare earth elements in the initially charged sludge have been chlorinated to corresponding trichlorides. This means that some part of rare earth trichlorides is not recovered at the higher temperature collector. A part of un-recovered rare earth trichlorides is mixed in the lower temperature deposit. Therefore, if $FeCl_2$, deposited in the lower temperature collector, is reused at the next batch, the rare earths in $FeCl_2$ deposit can be recovered. Another part of un-recovered rare earth trichlorides may deposit on the graphite tube adjacent to the higher temperature collector or on the surface of inner stainless steel tube surrounding the carbon parts.

4.1.3   Chlorination of other elements in the sludge

The sludge contains small amounts of Al and Co as additional elements. After the experiments, aluminum was not detected in the residue by the XRF analysis. The amount of boron in the graphite crucible decreases slightly after the experiments as shown in Table 3(b). These observations suggest that a part of boron and almost all aluminum in the sludge are chlorinated by $FeCl_2$. It should be noted that formation of BCl_3 and $AlCl_3$ is possible from thermodynamic viewpoint as it can be deduced from Fig. 1. Actually, the aluminum chloride deposit was found on the inner surface of the exhaust port (Fig. 6) which was kept at room temperature. It is expected that boron trichloride is also trapped at the cold trap because the boiling point of boron trichloride (b.p. 286 K) is lower than room temperature. In the experiments, however, the concentration of boron in the cold trap was lower than the detection limit of ICP analyzer, while significant concentration of boron is obtained in the lower temperature deposit that consists mainly of $FeCl_2$ as shown in Table 2. The reason why boron chloride deposits with $FeCl_2$ at temperatures higher (> 413 K) than the boiling point of BCl_3 (286 K) is not clear yet. But such a phenomenon may be caused by formation of complex chloride consisting of BCl_3 and $FeCl_2$, although such a complex formation is not reported as far as we know. Cobalt was not found in the deposit at both the higher and lower temperature collectors, and in the deposit at the exhaust port, while it was detected in the residue in the graphite crucible. Thus, it can be concluded that cobalt in the sludge is not chlorinated by $FeCl_2$, which is understandable qualitatively from thermodynamic viewpoint.

As shown in Table 3(b), the increase in the amount of iron in the residue is 2.54 g. This value is significantly larger than the corresponding stoichiometric value, 0.78 g, calculated for the chlorination reaction (eqs. (1) and (2)) of rare earth elements in the sludge. A part of the excess iron formation is caused by chlorination of Al and B in the sludge. However, even with considering the chlorination, the experimentally obtained amount of iron is still larger than the theoretically estimated value. As another reason, the excess iron formation may be caused by the reaction $H_2O(g) + FeCl_2(l,g) + C(s) \rightarrow Fe(s) + 2HCl(g) + CO(g)$. The H_2O probably comes from the decomposition reaction of $Nd(OH)_3$ that is confirmed by the XRD analysis in the sludge.

4.2   Conversion of trichloride to oxide

As described in the above sections, a mixture of neodymium and dysprosium chlorides of fairly high purity, 99.2%, was obtained in the present experiments. The rare earth chlorides can be directly used as raw material for the molten salt electrolysis or metallothermic reduction. However, in practice, almost all rare earth metals are presently produced by the rare earth oxide electrolysis. Thus, if the chlorides are supplied as raw material for conventional process, we have to convert the obtained chlorides to oxides. In a flow containing oxygen gas, the conversion of the rare earth chlorides to oxychlorides is relatively easy. But, converting the rare earth oxychlorides to the corresponding oxides in a flow of dry air or pure O_2 requires very low partial pressure of chlorine. For example in Nd–O–Cl system, the required partial pressure of chlorine, p_{Cl_2}, must be lower than 2×10^{-5} MPa (in dry air) or 3×10^{-5} MPa (in pure O_2) at 1273 K.[14] Such a low chlorine pressure makes removing chlorine gas from the oxychloride phase practically impossible because of small driving force for the gas-side mass transfer of chlorine gas.

To investigate a possibility for the conversion of neodymium trichloride to oxides under pure O_2 atmosphere, 3.0 g of neodymium trichloride hexahydrate ($NdCl_3·6H_2O$) was heated at 1273 K for 24 h in an alumina boat under 99.9999% O_2 stream condition (40 cm^3/min). A typical example of the X-ray diffraction pattern of the product after the experiments is shown in Fig. 9(a). The abundant phase is the neodymium oxychloride (NdOCl), and the neodymium oxide phase (Nd_2O_3) is rather minor. This result proves that it is not easy to convert neodymium oxychloride to oxide completely under pure oxygen or dry air atmosphere.

However, when a relatively large amount of water coexists in the gas phase, the following hydrolysis reaction is expected.

$$2NdOCl(s) + H_2O(g) \rightarrow Nd_2O_3(s) + 2HCl(g) \qquad (3)$$

When the partial pressure of H_2O is 4.7×10^{-2} MPa that corresponds to the vapor pressure of water at 353 K (80°C), the calculated equilibrium partial pressure of HCl at 1273 K is 5×10^{-3} MPa. This value is considerably higher than the partial pressure of Cl_2 in the case of dry air or pure O_2 atmosphere ($\sim 10^{-5}$ MPa). Therefore, a significantly higher driving force for the rate of evaporation of HCl from the oxychlo-
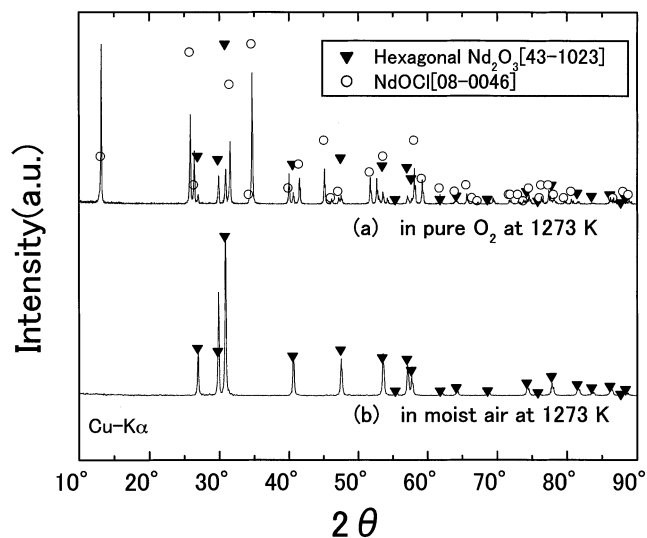

Fig. 9   X-ray diffraction patterns of the product after heating neodymium trichloride hexahydrate in pure O_2 at 1273 K and in moist air at 1273 K.

ride phase can be expected. Thus, in this case, the conversion of chloride to oxide in moist air can be kinetically easier than in dry air or pure O$_2$ under the same fluid dynamic conditions. Some researchers have studied the dehydration process of hydrated rare earth chlorides by a such thermal analysis as TG (Thermogravimetry) and DTA (Differential Thermal Analysis).[18–20] They observed that the conversion of rare earth chloride to oxide proceeded in air that was not dried although the mass of their samples placed in a thermal analysis apparatus was very small (less than 100 mg) and some products were mixture of oxychloride and oxide.

To confirm conversion of neodymium chloride hydrate to oxide by pyrohydrolysis, some trials were carried out. Neodymium chloride hexahydrate of 4.0 g was placed in a furnace, heated up to 1273 K under moist air stream condition and kept at these conditions for 24 h. To make air humid, it was passed through pure water at 353 K. Then, the sample was hold at 1273 K for 6 h in dry air for the purpose of decomposition of partially formed Nd(OH)$_3$ and NdOOH to Nd$_2$O$_3$. The X-ray diffraction pattern of the product after the experiments is shown in Fig. 9(b). Only Nd$_2$O$_3$ phase can be detected in the pattern. The sample was also analyzed by the XRF analysis. As the results, no fluorescent X-ray related to chlorine is observed. Thus, it is concluded that neodymium chloride hydrate is completely converted to neodymium oxides under the moist air atmosphere. In other trial runs for samarium, yttrium and dysprosium chloride hydrates, XRD patterns of the reaction products showed that these chloride hydrates can be completely converted to the corresponding oxides by the pyrohydrolysis reaction.

4.3 Schemes for recycling process of magnet sludge

The proposed method of selective chlorination by FeCl$_2$ in combination with the conventional electrolysis of oxide for recycling process of the magnet sludge requires treating HCl produced in the conversion reaction (eq. (3)). Here, it is worth discussing the use of HCl as the chlorination reagent for metallic iron which left in the residue of magnet sludge after separation of the rare earth elements. Both gaseous HCl and hydrochloric acid can chlorinate metallic iron to iron dichloride. Gaseous HCl can chlorinate iron metal to iron dichloride at elevated temperatures. It is also possible to synthesize FeCl$_2$ by dissolving the metal iron into a hydrochloric acid solution and following dehydration of the iron dichloride hydrate under dry HCl gas atmosphere. As an alternative method, iron dichloride methanol solvates are formed when metal iron is dissolved into hydrochloric acid with a large amount of methanol and the solution is evaporated.[21] As the iron dichloride methanol solvates decompose into FeCl$_2$ and methanol at 433 K under vacuum, the dehydration under dry HCl gas atmosphere is not necessary. Consequently, we can construct a new scheme for recycling process of the rare earth magnet sludge as shown in Fig. 10. In the new process, a circulation of chlorine can be achieved. During this circulation, only carbon and water are consumed, and the products are Ln$_2$O$_3$, H$_2$, CO or CO$_2$, and Fe-alloy. These products are not toxic for environment. A part of Fe-alloy may be re-used as raw material to synthesize FeCl$_2$. The obtained Ln$_2$O$_3$ can be used as raw material in the conventional electrolysis process
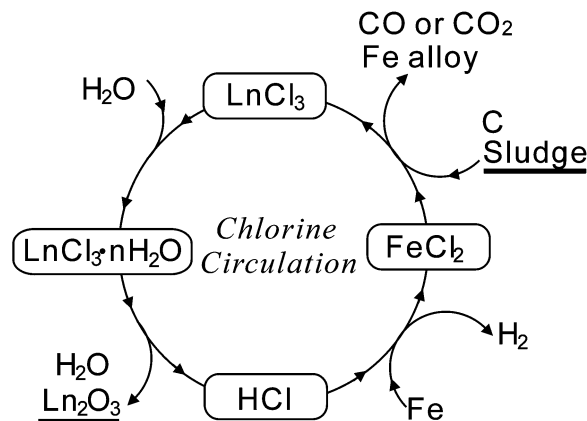

Fig. 10 New proposal of recycling process for rare earth magnet sludge. During the process, only water and carbon are consumed. The products are Ln$_2$O$_3$, Fe-Alloy, CO or CO$_2$ and H$_2$ gas. The obtained rare earth oxide can be directly used as raw material for the oxide electrolysis.

without any pretreatment.

4.4 Outline scheme of recycling for mixture of different types of magnets

Various types of rare earth magnets are produced for practical use in recent years. In addition to sintered or bonded neodymium magnets, rare earth magnets, containing samarium (Sm–Co and Sm–Fe–N), are often used as sintered or bonded magnets. In the near future, a waste consisting a mixture of different types of rare earth magnets will generate.

As expected from the thermodynamic consideration and results of the present study, FeCl$_2$ can be also used as a chlorination reagent for rare earth elements in the Sm–Co magnet without chlorination of cobalt. In addition, we believe that the proposed recycling process can be also applied for the bonded magnet waste. The bonded magnet consists of rare earth alloy powder and epoxy resin of several mass percent in composition. When the epoxy resin is heated under an inert atmosphere, the epoxy resin thermally decomposes into various gaseous organic compounds and residual char.[22] After the decomposition, the mixture of residual char and rare earth magnet powder is mixed with FeCl$_2$ and heated. Then, rare earth elements in the magnet powder will be extracted into salt phase. It should be noted that the residual char after heating under inert atmosphere acts probably as de-oxidation reagent like the activated carbon used in the present study.

Thus, a mixture of rare earth chlorides, containing samarium, neodymium and dysprosium, can be recovered from the waste of mixture of different type magnets by the proposed recycling process using FeCl$_2$. Subsequently, we have to separate samarium from neodymium and dysprosium. In previous studies, we have investigated a new dry separation process for rare earth chlorides by vacuum distillation combined with selective reduction.[23,24] The similar idea of rare earth separation by using the selective reduction was also suggested by Sato and Nanjo.[11] According to our investigation, the chloride mixture of samarium and neodymium can be separated into samarium-enriched and neodymium-enriched chloride by the vacuum distillation combined with selective reduction. Apparent separation factor between neodymium and samarium in the new dry separation process is $\beta_{\text{Sm/Nd}} = 570$,

which is considerably larger than the separation factor of 2.2 to 9.6 reported for the conventional solvent extraction process. We believe that the new dry separation process can provide the separation of samarium and dysprosium chlorides although the process has not been demonstrated (the results on the separation of samarium and dysprosium in an iodide system are already reported[25]). Therefore, each rare earth can be recovered separately from a waste of mixture of the rare earth magnets by combining the selective reduction-vacuum distillation method and the proposed recycling process.

5. Conclusions

The rare earths in the sludge was selectively chlorinated by $FeCl_2$ with activated carbon as a de-oxidation reagent without chlorination of iron. The rare earth chloride was separated from Fe-alloy and the excess of $FeCl_2$ by the vacuum distillation. The experimental findings are as follows.

(1)   96% of neodymium and 94% of dysprosium in the sludge was extracted into chloride phase by heating with $FeCl_2$ and activated carbon at 1073 K for 12 h.

(2)   The mixture of neodymium and dysprosium trichloride of 99.2% purity (cationic mass percent) was recovered by the vacuum distillation with the yield of 76% to the amount of the initially charged sludge.

(3)   The rare earth chloride hydrates were converted to corresponding oxides by pyrohydrolysis reaction without formation of rare earth oxychloride. The produced HCl can chlorinate metallic iron to $FeCl_2$.

Above findings give a possibility for establishing a new efficient recycling process for rare earth magnet as a chlorine circulation type process. During the process, only carbon and water are consumed, and the products are rare earth oxide, Fe-alloy and gaseous hydrogen and carbon oxide. The process does not produce any toxic pollutants and wastewater in principle. Moreover, the obtained rare earth oxides can be directly used as raw materials in the oxide electrolysis, which is main industrial reduction process at the present.

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